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BIMONTHLY REPORT

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on the

THERMOELECTRIC GENERATOR PROJECT

Covering the Period

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ABSTRACT

The problems attendant upon the development of a twenty-couple thermoelectric generator using lead telluride and zinc antimonide as the active materials have been divided into those of measurement and those of device design. In the first category, progress is reported in the design and construction of equipment to supply data which will permit greater accuracy in the prediction of the thermoelectric efficiency of the completed device. Device-design studies are in progress, with the objective of improving the thermal and electrical design of the completed assembly. Ingots of lead telluride have been produced, and a preliminary investigation of bonding methods has been performed.

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I. PURPOSE OF THE STUDY

The purpose of this project is to extend the technology of small, portable thermoelectric generators to include a twenty-couple zinc antimonide-lead telluride generator which can serve as a prototype for the construction of larger assemblies.

II. INTRODUCTION

It is well recognized that two factors limit the efficiency of conversion of heat to electricity by thermoelectric generators: first, the materials employed and the temperature range in which they are used; and second, the mechanical and electrical design of the device which utilizes the materials. The temperatures and materials selected set an upper limit on the efficiency of the conversion, within which limit careful design and assembly can lead to a device of greater or lesser utility.

In the course of the studies which led to the current project, the emphasis was on proving the feasibility of thermoelectric power generation. Emphasis was mainly on the selection of materials and temperatures of operation, with only sufficient attention given the design of the completed device to assure the demonstration of its utility. The present project embodies several aspects whose aim is the improvement of the efficiency of the thermal and electrical design of the completed device. These aspects may be categorized as measurement and device-design activities.

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III. MEASUREMENTS

The need for improvement in the extent and number of measurements performed on the materials employed in the projected device may best be appreciated by inspection of the equation defining its optimum efficiency:

$$\eta = (1 - T_c/T_h) \frac{(1 + Z\bar{T})^{1/2} - 1}{(1 + Z\bar{T})^{1/2} + T_c/T_h}$$

in which $Z = \frac{S^2}{\rho k}$ for a given material,

and $\bar{T} = (T_h + T_c)/2$ (\bar{T} is the mean temperature)

where η is the overall efficiency,

T_c is the cold-junction temperature,

T_h is the hot-junction temperature,

Z is the figure of merit of the material,

S is the Seebeck coefficient of the material,

ρ is its electrical resistivity,

and k is its thermal conductivity.

The equation above is exact only when the figure of merit is invariant with temperature. This is nearly true when temperature differences are small, but errors become appreciable when the temperature difference is as large as in the present application ($T_h = 350^\circ\text{C}$; $T_c = 80\text{-}100^\circ\text{C}$).

In order to correct for any changes in the figure of merit which will result from the elevation of the temperature, it is necessary

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that accurate information be obtained over the entire temperature range concerning the Seebeck coefficient, resistivity, and thermal conductivity of the lead telluride and zinc antimonide to be employed. To this end, much of the activity during this reporting period was devoted to the design of equipment for such measurements. Because it is equally desirable to be able to ascertain the homogeneity of a given specimen of thermoelectric material, equipment has also been designed which can detect variations in the electrical resistivity and Seebeck coefficient along the length of a bar of such material. This equipment, referred to as a "profiler", has been constructed and is ready for operation. Its design is such that it can be modified to determine the resistance between a piece of thermoelectric material and the metallic contact piece to which it is bonded. The necessity for such measurements is discussed in the next section.

IV. DEVICE DESIGN

The thermoelectric generators constructed during the studies which led to the present project never exhibited the efficiency predicted for the materials (about 3.5 per cent for zinc antimonide and constantan with the temperatures specified above). Rather, the efficiency actually observed was no greater than 2.0 to 2.2 per cent. Part of the explanation for this difference lies in the use of room-temperature data to predict the maximum efficiency obtainable with these materials. The remainder of the discrepancy must be attributed to

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factors of device design. Some of the aspects of this type of problem are described below.

1. Lead resistance. The wires which carried the electrical power to the exterior of previous devices were of nickel, for ease in affixing them to the ends of the generator itself. The use of this material resulted in the introduction of an electrical resistance nearly one-fourth that of the entire generator, and a consequent reduction in its power output. Means must be contrived for the use of leads which do not have this undesirable property.

2. Contact resistance. Although means have been developed for production of bonds between zinc antimonide and its contact pieces which can introduce as little as eight per cent additional electrical resistance, measurement of the resistance of individual contacts was not, heretofore, considered necessary. It is therefore likely that individual bonds may have exhibited excessive resistance, with corresponding adverse effects on the observed efficiency. In prior thermoelectric generators, the use of constantan permitted half the total number of bonds to be made by welding. In the current device, all eighty contacts will be made by an alloying process. The use of the profiler, described above, will permit the measurement of the resistance of each contact, reducing the possibility of loss of efficiency by this means.

3. Thermal contact. The use of less-than-atmospheric pressure in the interior of previous devices was intended, partly,

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to assure good thermal contact between the generator itself and the housing. Additional assurance of good thermal contact was obtained on the low-temperature side by application of an adhesive resin. The possible effects of warping of the hot side could not be measured until the life-testing of previous devices was completed. These measurements are to be made, and the information gained thereby employed to improve the reliability of the thermal contact between the hot junctions of the generator and its container.

4. Container design. One of the two previously-constructed generators failed because of melting of the solder used to provide a hermetic seal. This accident took place when the cooling water fell to an inadequate level in the upper pan. Recurrence of this type of catastrophe was prevented in the second model by the use of a higher-melting solder. This remedy does not, however, obviate the large thermal short-circuit afforded the thermoelectric generator by its container. The evident loss of efficiency can be reduced by changes in the geometry of the pans, resulting in a more efficient and more reliable device.

During the current reporting period, the activity in the field of device design was limited to the formulation of plans for attack of the several problems. In successive periods, this portion of the project will receive major emphasis.

V. MATERIALS

Ingots of n-type lead telluride containing 0.1 per cent of bismuth have been prepared. It has been found that recasting of

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this material to shapes suitable for use in thermoelectric generators may be accomplished by means similar to those used for recasting of zinc antimonide. A preliminary investigation of bonding techniques has shown that use of 5 per cent indium - 95 per cent lead alloy results in bonds of adequate mechanical strength.

VI. PLANS FOR NEXT REPORTING PERIOD

It is hoped that the equipment described in the section on measurements will be placed in operation. Device design studies will include a detailed analysis of the warping of the containers used for the previous two thermoelectric generators. It is expected that an experimental verification of the quoted value of the coefficient of thermal expansion of lead telluride (24×10^{-6} per degree) can be performed. This will permit refinements to be made in the mechanical design of the containers. In addition to the foregoing, lead telluride and zinc antimonide will be prepared in quantities sufficient for preparation of bonded samples.

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